How carbon black affects electrical properties

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Carbon black is one of the world’s most versatile materials. Discovered in ancient China and used initially for its black pigmenting properties, today carbon black is finding new and more diverse applications in many industrial processes.

More than 70 percent of carbon black produced worldwide is used to provide reinforcement for rubber compounds such as tires and manufactured rubber goods.

It is also used as a pigment for inks, paints, plastics and other items where black color is desired. In addition to providing reinforcement and color to rubber compounds and plastics, carbon black protects these materials from deteriorating UV radiation.

Recently, new and growing “green” energy industries are also benefiting from using carbon black. An example of this is carbon blacks used as a catalyst support in fuel cell assemblies.

One of carbon black’s unique properties will be examined in more detail in this paper, namely its ability to affect the electrical properties of a compound when used as the filler.

This phenomenon is based on the fact that carbon black is a very finely divided material with particle size in the range of nanometers which are electrically conductive. Carbon black filled rubber compounds are good composites in which to study the effect of the filler on material electrical properties.

From an electrical point of view, rubber compounds consist of two interpenetrated networks: the conductive carbon black network and the resistive polymer network. These differences in electrical properties lead to great opportunities in designing rubber compounds with the range of resistivity stretching more than 16 orders of magnitude.

There are multiple objectives that the authors would like to accomplish in this paper. First, to demonstrate a simple technique of measuring resistance and resistivity of rubber compounds that can be employed in virtually any laboratory without the necessity for sophisticated equipment.

Next, to establish the resistivity baseline by discussing the intrinsic resistivity of carbon black itself. The main body of the paper will focus on the influence of different grades of carbon black on rubber compound electrical properties. The effect of loading, polymer type and mixing condition also will be discussed.

Finally, this paper will show the examples that can be easily implemented in the production environment.
Experimentation technique
While resistance and resistivity are related properties, they are not synonymous. Resistivity is an intrinsic material property, which therefore is independent of the sample geometry.

Resistivity depends not only on the material but also on the geometry of the tested sample. When making volume resistivity (ρ) measurements, the measured resistivity (ρ) is multiplied by the cross-sectional area (S) of the sample perpendicular to the current flow, and divided by the path length of the current (d) (see Fig. 1).

The level of volume resistivity usually will both be used because conductivity, or, is simply the reciprocal of resistivity, ρ. (See Equations 1 and 2).

There are many established methods to measure the resistivity of various materials. These are thoroughly described in the literature and documented as ASTM methods.

One of the ASTM procedures dealing with rubber compound resistivity is designated as ASTM D991. This procedure requires a specially designed sample holder/measuring device machined to exact specifications. It also requires a specific sample size, which often is not readily available. Results obtained from the technique described in this procedure also can be affected by the contact resistance and surface currents. Additionally, the effect of strain caused by the pressure electrodes on rubber compound resistivity is not accounted for in ASTM D991.

On the other hand, the ASTM D991 procedure being a classical four-point method does account for the measuring wire’s resistance.

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quire this classical technique which is necessary, however, in cases of highly conductive samples.
As we would like to demonstrate later in this section, a better and simpler techni-
que can be used to achieve very accurate results.
Because of the fact that carbon black filled rubber compounds consist of two in-
terpenetrated networks, each having drastically different resistivities, the re-
sistivity of the final rubber product can range over almost 16 orders of mag-
titude. Fortunately the majority of rubber compounds have resistivities between 10$^2$ and 10$^4$ Ωcm.

There are very specific experimental challenges depending on the resistivity level of the sample under investigation.
On the upper side of the spectrum are unfilled polymers with resistivity reach-
ing 10$^{10}$ Ωm. Such a high level of resistiv-
ity is difficult to measure without so-
plicated equipment and techniques.
When dealing with very high resistivity we have to account for the surface cur-
rents, humidity, and temperature and be able to measure the currents in the femtoamps range (10$^{-15}$ A).
Compounds having low resistivity are simpler to work with, but one has to ac-
count for the resistance of the voltage source and connecting wires.
As shown in Equation 1, in order to calculate the volume resistivity, one has to measure the resistance (R = V/I) of the sample. The sample geometry has to be simple enough the accurate meas-
urements of the cross section area (S) and the length of the sample (d) can be
obtained. Examples of such geometries include cylindrical shapes and rectangular shapes.

Examples of curing molds that can be used for sample preparation include the rebound mold (as described in ASTM D1054), compression set mold (D385), Goodrich flex or Firestone flex mold (D623), or even the tensile pad mold (D412).

Some examples are presented in Fig. 2. Using samples with different geome-
try can sometimes help to mitigate the inadequacy of measuring devices. We will elaborate on this more thoroughly later in this paper.

One of the most important steps in sample preparation is the application of the electrodes. Neglecting this step leads to increased values of resistance/resistiv-
ity as is seen in the example presented in Fig. 3. This increase is caused by the contact resistance phenomena.

There are several simple methods to improve the electrical contact of elec-
trodes with rubber. In our experiment, the gold sputtering system Hummer VII

As shown in Fig. 6. The two-dimensional represen-
tation of the rubber samples filled with the same mass of N600 series carbon black (right side) and N100 series carbon black (left side).

Fig. 6. The two-dimensional representation of the rubber samples filled with the same mass of N600 series carbon black (right side) and N100 series carbon black (left side).

As shown in Fig. 7, TEM images of carbon black in-rubber network at 10, 30 and 50 phr loading. The volume resistivity curve represents three resistivity zones.

Before Percolation (10 phr)

At Percolation (30 phr)

After Percolation (50 phr)

Carbon Black Loading [phr]

Carbon Black Loading [phr]

Intrinsic volume resistivity
In order to understand how and why carbon black impacts compound electrical properties, we must first examine the intrinsic volume resistivity of carbon black itself.
Carbon black can be produced using a number of available processes. Almost all carbon black used today is manufac-
tured using the furnace process. Materi-
al produced in this way will have specific surface areas measured by the ni-
trogen adsorption BET technique in the range between 20 and 1000 m$^2$/g.
The primary particle size, measured by transmission electron microscopy (TEM), can vary between 10 and 100 nm. The aggregate size approximated by the Stokes diameter and obtained from
resistivity will be slightly below $10^{-2}$ concentration of oxygen surface groups. Ment processes will have higher intrinsic resistivity. The schematic of the apparatus employed for such measurements is resistivity. The schematic of the apparatus employed for such measurements is resistivity. The schematic of the apparatus employed for such measurements is resistivity. The schematic of the apparatus employed for such measurements is resistivity.

The experiments performed on many grades of carbon black, including conductive grades, as a function of compression pressure (to reduce the void volume between aggregates) shows that all carbon blacks fail in the same range of volume resistivity as demonstrated in Fig. 4.

This range is between $10^{-1}$ - $10^{-3}$ ohm. Carbon blacks oxidized by post-treatment processes will have higher intrinsic volume resistivity caused by large concentration of oxygen surface groups. Volume resistivity of graphitized carbon black will be slightly below $10^{-3}$ ohm.

These two examples however do not change the final conclusion as they indicate only that the post treatment process can influence carbon black volume resistivity. The schematic of the apparatus employed for such measurements is presented in Fig. 5.

Measuring pure/intrinsic carbon black resistivity is relatively complicated. The results depend how completely the sample was compressed to reduce the void volume between aggregates and ultimately how the direct contact between aggregate surfaces is maximized.

There is, however, a limit to how low the intrinsic resistivity of conventionally produced carbon black can be. This limit is set by the resistivity of the pure crystalline graphite (for example HOPG) measured parallel to the plane. This limit is set at 10-3 ohm. Other carbon materials, like metal doped carbon black nanotubes where quantum mechanical mechanism plays a role, could possibly break this barrier.

It may seem to be contradictory, at first, when we state that all furnace blacks will have the level of their intrinsic volume resistivity set at $10^{-3}$ ohm. Why then are some of these blacks called "conductive" while the others are not? It should be made clear that while all carbon blacks are conductive, the ones marketed as "conductive" can develop conductive networks at much lower loadings in the resistive polymer.

The difference between these carbon blacks depends on the distribution and effective volume they occupy in the media in which they are dispersed, such as rubber or plastic.

Since rubber compounding is performed using the mass of filler, the highly porous filler black will occupy a larger volume in rubber as compared to non-porous conventional carbon blacks. Examples of how effective the conductive blacks are in reducing compound resistivity will be presented in the following sections.

Discussion

It is well documented in the literature that types of carbon black (carbon black loading, type of polymer and mixing practices all affect rubber compound volume resistivity). The following section will present new data obtained for ASTM and specialty blacks designed to significantly impact compound resistivity.

The blacks specifically mentioned are Sidcon 119, designed to provide high conductivity to rubber compounds at very low loadings, and Sidcon 119 and 419, slightly less conductive alternatives designed for easier processing.

Carbon black type and loading experiments

The influence of carbon black type and loading on rubber compound volume resistivity is quite significant. In order to focus on the background for this discussion let's consider first what is happening when voltage is applied to a rubber sample.

The current, $I = V/R$, is flowing through the path of the least resistance, which in this case is through a conductive carbon black network. When no continuous carbon black network exists throughout the sample, the current flow is scattered. This exercise will illustrate how different grades with different specific surface areas will affect compound resistivity.

If we assume, that N600 series carbon black aggregates are about 230 nm in diameter and N100 series black aggregates are 80 nm in diameter, we will need 72 aggregates of N100 series to have the same mass as three aggregates of N600 series.

When these larger and smaller aggregates are separately distributed in equivalent volumes of rubber, there are very significant differences in the formation of a continuous path from one side to the other side of the hypothetical sample. A two-dimensional representation of this phenomenon is plotted in Fig. 6. Thus one should expect a strong dependence of volume resistivity on specific surface area of carbon black. Larger surface area carbon blacks should provide more conductivity to rubber compounds because of their much smaller particle and aggregate size.

As mentioned above and illustrated in the graph below (Fig. 7) carbon black loading has a pronounced effect on rubber compound volume resistivity.

The transmission electron microscopy (TEM) photographs below confirm the changes in carbon black network density and corresponding with it, the number of percolated sub-networks. These pictures allow for easy visualization of the effect of filler percolation.

The corresponding graph representing volume resistivity shows the three resistivity zones: the resistive zone, percolation zone and conductive zone.

The effect of carbon black type on rubber compound resistivity values also can be seen as the effect of specific surface area on compound resistivity.

In the following example, conductive grades Sidcon 139 (high specific surface area), Sidcon 119 (medium specific surface) and N550 (low specific surface area) were measured. For each of the three grades the volume resistivity was measured following a 4 point Kelvin probe method. The data is presented in Fig. 8.
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cane area) and Sidcon 419 (low specific surface area) produced by Sid Richardson Carbon & Energy Co. will be compared to selected ASTM grades as well as with a widely used conductive black, N472. Selected analytical properties of carbon blacks used in this experiment are presented in Table I.

The purpose of so-called “conductive” carbon black grades is to provide the desired conductivity to the rubber compounds or plastic materials at very low loading (concentrations).

The volume resistivity data as a function of carbon black loading are represented in Fig. 8. All samples were prepared according to the ASTM D3191 formula with solution SBR as the polymer.

Carbon black loadings used in this experiment varied widely depending on the grade of carbon black. As expected, the resistivity values decrease rapidly with carbon black loading especially for high surface area and conductive carbon blacks.

Fig. 13. Selected rubber properties obtained in ASTM D3191 formulation for various conductive carbon blacks from the example in Fig. 12.

The differences between different grades of carbon blacks are very pronounced at each loading. Carcass grades like N774 will not reach percolation threshold even with loadings as high as 60 phr. The same holds true for other N700 series grades.

Rubber compounds filled with these grades remain resistive up to at least 60 phr. N600 and N500 series (the N550 presented here) behaves very similarly. However, at the higher loadings they reach lower resistivity levels as compared to N700 series.

Even at very low loadings such as 20 phr, Sidcon 159 brings the rubber compound to the conductive zone with resistivity in the range of 10^11 ohm.

As a high surface area and high porosity carbon black, Sidcon 159 will have a significant impact on rubber compound electrical properties. It will also impact rubber compound processing and dynamic properties. A lower surface area carbon black easier to process in Sidcon 119, which requires slightly higher loadings to obtain the same level of resistivity with improved rubber processing and dynamic properties as Sidcon 159. When the compound processing is very important and a required level of resistivity is not extremely low, Sidcon 419 is the best candidate.

One carbon black provides excellent processing properties similar to extrusion grades and at the same time impacts the electrical properties significantly as compared to N500 or N600 series carbon blacks.

As can be seen from the above example the advantage of conductive grades is most pronounced at low loadings. Fig. 9 represents the relationship between resistivity and specific surface area. The relationship is clear, which is expected based on all of the information presented above.

However, by closely examining Fig. 9 one can immediately note that Sidcon 119 provides lower resistivity to rubber compounds than one would expect from the specific surface area data. This indicates that other properties of carbon black may also affect resistivity.

After examining the effect of carbon black loading and specific surface area on rubber compound resistivity, it becomes clear that higher loading and higher surface area blacks will provide lower volume resistivity.

The high structure of the carbon blacks (with increased degree of branching of the aggregates) will lower resistivity by increasing the propensity for the electron tunneling at lower loadings.

Use of conductive grades can magnify these effects by several orders of magnitude. In the following section, other ways to affect compound resistivity will be discussed.

Polymer type dependence

As demonstrated in previous work, polymer type and compound formulation play a very important role in achieving the required level of volume resistivity. There are a number of reasons why different polymers or formulations lead to different levels of resistivity.

One of the most important among them is the compatibility between filler and polymer. An incompatible system will form areas of unfilled polymers and undispersed filler.

The filler-polymer interactions are weak or non-existing in such cases. This situation leads usually to poor dispersion and often lower volume resistivity.

An example of this can be found when the compounding is done with blends of polymers having different affinities for carbon black.

In this case, it was found that the carbon black will be concentrated at the interface of two polymer phases, usually lowering compound resistivity.

The example in Fig. 10 illustrates such a situation; when solution SBR and natural rubber were used at different ratios and N772 carbon black was used at different loadings.

To demonstrate the performance of the Sidcon 159, Sidcon 119 and other carbon blacks used in the previous example, several different “model” formulations were investigated.

The “model belt” formula, the “model cable shield” formula and the ASTM D3568 EPDM formula were used with only 30 phr loading of carbon black (for formulation details please refer to Table II).

The results are presented in Fig. 11.

The levels of volume resistivity observed in these formulations are compared to the ASTM D3191 formulation at various carbon black loadings.

Table II. Rubber formulas.

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<tr>
<th>Ingredient</th>
<th>EPDM 50 phr</th>
<th>SBR 100 phr</th>
<th>EVA 100 phr</th>
<th>Natural Rubber 100 phr</th>
<th>SBR 1500 100 phr</th>
<th>Natural SBR 100 phr</th>
<th>SBR 50 phr 30 phr</th>
<th>N550 40 phr</th>
<th>Zinc Oxide 3 phr</th>
<th>Stearic Acid 1.5 phr</th>
<th>TMTD 1.5 phr</th>
<th>MBT 0.5 phr</th>
<th>MBTS 0.6 phr</th>
<th>FBBS 0.5 phr</th>
<th>Paraflin 18.8 phr</th>
<th>Furfur 7.5 phr</th>
<th>Aromatic 0.75 phr</th>
<th>Alumina 0.75 phr</th>
<th>Peroxide 1.1 phr</th>
<th>Activator 0.6 phr</th>
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Fig. 14. The effect of dispersion (mixing time) on volume resistivity. Data obtained for ASTM D3191 filled with 50 phr N660.
the majority of conducting electrons are flowing through the relatively poorly dispersed carbon black network. With increasing mixing time the N660 aggregates separate, and the number of connections between them decrease, causing the resistivity to increase.

This resistivity result has a significant practical application in compounding rubber for a given resistivity level. It shows that not only the type of carbon black, but also carbon black loading can alter the level of resistivity. In this example the changes were significant: 10 orders of magnitude. For practical purposes, poorer dispersion will lead to lower resistivity values. Because it is not always practical in the factory environment to change the mixing time, other techniques may be employed. One possible technique is to change the order of how carbon black is added to the mixer during the mixing process.

Typically, in the masterbatch stage of mixing, the aggregate structure is black to the mixer. Next, in the final stage of mixing, the conductive black is added. The chart in Fig. 15 represents the sequence when conductive black was added in the masterbatch stage of mixing. Notice how this was then added during the final stage.

The volume resistivity was lowered one order of magnitude despite the range of loadings. If further reduction in resistivity is necessary, the conductive carbon black could be added in another stage of productive stage mixing, further reducing dispersion and decreasing resistivity.

Summary and conclusions
One of the most important points the authors attempted to accomplish in this paper was to present a simple technique to measure the volume resistivity of rubber compounds which can be employed in the majority of rubber laboratories. This procedure uses standard curing molds for sample preparation and the measuring instrumentation is just a simple multimeter.

Also, by changing the sample geometry, the range of resistivities can be measured that cover the entire orders of magnitude. Results that have been used for real carbon black filled rubber compounds.

Because carbon black provides the conductivity in rubber compounds, forming the conductive network within the elastomer matrix, the authors presented the measurements of the intrinsic volume resistivity of carbon black itself. The resistivity was established to be in the order of 10^15 Ω cm and is the same for all carbon blacks including conductive grades. The schematic of the aggregates designed for these measurements was presented.

Volume resistivity measurements of rubber compounds presented in this paper were designed to demonstrate how resistivity depends on carbon black loading, carbon black grade, carbon black specific surface area and structure. It was shown that resistivity decreases sharply with increased carbon black loading and filters of increased specific surface area of carbon black.

The performance of conductive black also was discussed. The authors strated how conductive grades like Sidcon 159, Sidcon 119 and Sidcon 419 can influence compound resistivity as well zzr other properties. The range of Sidcon conductive grades presented in this paper proved the importance to the rubber compounder charged with designing rubber compounds with low resistivity and at the same time maintaining the required rubber processing and dynamic properties.

The influence on polymer type was also discussed. Next, the authors presented examples of how a rubber engineer or compounder could use various mixing and compounding techniques to further reduce or control the compound resistivity.

It was shown that poor dispersion usually leads to lower resistivity. Dispersion can be reduced by reducing mixing time and/or adding the conductive carbon black in the last, productive stage of mixing.

This paper focused on the influence of carbon black on compound volume resistivity, but it should be noted that many other important factors can influence this property. These include but are not limited to: temperature, humidity, applied pressure and strain history of the sample.

This paper also illustrated the significant influence that carbon black can have on compounds beyond its well known role as a reinforcing filler.

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References

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Fig. 15. The volume resistivity versus conductive carbon black loading obtained for two different mixing sequences as described in the graph legend.