Research article

Influence of chemical composition, porosity and fractal dimension on the electrical conductivity of carbon blacks

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ABSTRACT

Carbonaceous materials analyzed in this investigation were six nanometric particle size carbon blacks. Carbons were texturally characterized by gas adsorption (N2, 77 K), helium and mercury density and mercury porosimetry measurements. Electrical conductivity was determined by impedance spectroscopy, at room temperature. Several works related to the electrical conductivity and to textural parameters of carbon blacks, such as: porosity, specific surface area, etc., have been carried out. However, there are a type of parameters, such as the fractal dimension, the percentage of macropores, the particle size, or the packing density, that are also related to the electrical conductivity, but they have not been previously investigated. In this work, it has been researched how the increase in interparticle/intraparticle porosity decreases the electrical conductivity of the samples studied. Therefore, it is possible to conclude that in this study a complete research work on electrical conductivity has been carried out.

1. Introduction

Carbon materials (with composite materials composed of carbon) have a large number of electrical applications. These materials are relevant to be used in industrial applications related to electrical conductors, electrodes, electromagnetic reflection, heating, thermal conduction, thermoelectricity, sensing, electrical switching and electronic devices [1]. Carbon black is intrinsically a semiconductor, its electrical conductivity being in the range 10^{-1}-10^2 (ohm-cm)^{-1} [2]. Carbon black electrical conductivity is influenced by carbon nature and morphology, its aggregate and particle sizes and citations therein [2], its topology and chemistry surface [3,4], as well as level and nature of impurities on carbon outermost layer [2]. Other factors that affect the electrical conductivity are the surface and porosity. The fact is that most of high porosity conductive carbon blacks have been associated with the cleanness of their surface, having consequently smaller contact resistance [2].

Carbon black electrical conductivity can be raised by material compression since, by tunnelling effect, which the electrons can jump the air gap between the closely spaced carbon black aggregates. Accordingly, a large number of research works related to carbon black electrical conductivity measured under compression have been carried out [5, 6, 7, 8, 9]. In fact, the measurement of the electrical conductivity of compressed particles is a method applied beforehand to characterize granular and powder substance [10, 11, 12, 13], in particular carbon materials [14, 15, 16]. It was reported earlier by Espinola et al. [17] that the determination of the conductivity in porous and powdered substances was difficult. Just applying steady and established pressure the comparison of resistivity values can be made.

In the field of telecommunications, materials are being developed for shielding against electromagnetic interference (EIM) with carbon black. Recent studies inform about a flexible material, it is a lightweight microwave absorbing conductive polymer composite was manufactured by employing poly (ethylene-co-methyl acrylate) and ethylene octene copolymer (EMA/EOC) binary mix, as the matrix and multwall carbon nanotube carbon black (MWCNT/CB) hybrid padding as conductor part [18,19].

Diverse origins carbon blacks (i.e., plasma, partial combustion and activated) have been used in studies on electrical properties, by Probst and Grivei [20]. Under compression, changes may occur in the porous structure of the carbon, such as additional increases in electrical conduction. Owing to this fact, using a wide serie of six carbon blacks, the influence textural properties (i.e., surface area and porosity) on the
The obtained data of the elemental analysis of carbons used are shown in Table 1. These data shows valuable information on structural properties of the carbons. Thus, a high carbon to hydrogen ratio is compatible with a high aromatic character and with the fusion degree of benzene rings, whereas the opposite applies to the content of aliphatic structures.

In view of the results, the predominant structures in these carbon blacks are aromatic structures, as they present a high proportion of carbon and hydrogen in all series.

It is shown that the carbon content is lower down for BP1300 than for the other carbons. In contrast, contents of hydrogen, of nitrogen, and of oxygen are much higher for BP1300. The sulphur content is significantly higher for SV and lower for BP880. Finally, the total heteroatom content (THC) is similar for the majority of the carbons, except that for the case of BP1300 which is higher.

3.1.2. Textural measurements

All the adsorption isotherms and plots of mercury intrusion obtained for the carbons [30] are omitted from this study for the sake of brevity. From N2 isotherms, the specific carbons surface area was determined using the Brunauer, Emmett and Teller (BET) expression [36], to relative pressure ($P/P_0$) of 0.35 (to this $P/P_0$ value, BET plots shows straight lines) and using as $a_0$ value 16.2 Å [37, 38, 39]. From those isotherms too, micropore volume ($V_{\text{mi}}$) was determined considering it N2 volume adsorbed at $P/P_0 = 0.10$. Mesopores ($V_{\text{me}}$) and macropores ($V_{\text{ma}}$) volume was obtained using the curves of cumulative pore volume ($V_r$) versus pore radius ($r$) (mercury porosimetry): $V_{\text{me}} = V_{\text{cu}} (r = 37 \text{ Å}) - V_{\text{ma}}$ and $V_{\text{ma}} = V_{\text{cu}} (r = 250 \text{ Å})$.

Pore volume was determined using the following equation:

$$V_T = 1/\rho_{\text{hel}} - 1/\rho_{\text{hel}}$$

where $\rho_{\text{hel}}$ and $\rho_{\text{hel}}$ were mercury and helium densities. Total pore volume ($V_T$) was also calculated including $V_{\text{mi}}, V_{\text{me}}$ and $V_{\text{ma}}$. Table 2 shows $S_{\text{BET}}, V_{\text{mi}}, V_{\text{me}}, V_{\text{ma}}, \rho_{\text{hel}}, \rho_{\text{hel}}, V_T$ and $V_T$ values.
SBET values vary widely between 37-114 m²g⁻¹ for the V series (SV < V3 < V6) and 224–1443 m²g⁻¹ for the BP series (BP880 < BP1300 < BP2000) and so were higher for BP series, than for V series. The porosity volume values follow the same trend discussed in the previous paragraph.

Lately the quantitative description of the irregularity of solids surface has received has been the subject of several studies [39, 40, 41, 42]. Fractal dimension (D) supplies worthy data in this regard [43, 44, 45, 46]. Fractal dimension of a perfectly unwrinkled surface reaches a value of 2, while a very rough or irregular surface arrives to a level close to 3 [46]. In view of those results, surface morphology of carbon blacks presents numerous irregularities. Figure 2 presents SEM pictures of surfaces of a BP2000 sample.

### 3.2. Electrical conductivity

The study of electrical conductivity in carbon materials is considered to be a complex process. The works previously reported [2, 3, 4] have investigated the influence on the electrical conductivity of factors such as morphology, particle size, surface chemistry, structure (size/shape aggregate), porosity, etc. [13, 20].

Table 3 shows the values of σ measured for the carbons at P = 25 kPa (σ₁) and at P = 742 kPa (σ₂). σ₁ varies in sequence V3 > V6 > SV (serie V) and BP1300 > BP880 > BP2000 (serie BP) and σ₂ in the sequence SV > V3 > V6 (serie V) and BP1300 > BP880 > BP2000 (serie BP). σ₁ is lower for BP2000 than for the other carbons. The conductivity σ₂, it is markedly different for SV, BP1300 (high electrical conductivity), regarding to the rest of the samples V3, V6 and BP880 that present an intermediate electrical conductivity and BP2000 (low electrical conductivity) at the highest pressure. To have idea of the overall change produced in σ by compression of the carbons, the increase percentage value in electrical conductivity (PIEC), characterized as \(\frac{\sigma_2 - \sigma_1}{\sigma_1} \times 100\), are also set out in Table 3. It is seen that the greatest increase in the conductivity occurs for SV and, though to a lesser extent, for BP1300 and BP2000.

The increasing conductivity with pressure may be due to a decrease in the number of holes, an elastic or plastic deformation of the carbon beads, or even up to the breakdown of their structure.

#### 3.2.1. Influence of chemical composition

Carbon black are almost spherical primary particles, combined in aggregates. Several studies have pointed out that carbon blacks electrical conductivity is highly affected by structure, by specific surface area as well as by other properties [2, 6, 7, 8, 31, 34, 47, 48, 49].

### Table 1. Elemental analysis of carbon blacks.

| Carbon | C   | H   | N   | S   | O   | THP* |
|--------|-----|-----|-----|-----|-----|------|
| SV     | 96.01 | 0.37 | 0.17 | 2.02 | 1.58 | 3.77 |
| V3     | 96.58 | 0.34 | 0.17 | 1.29 | 1.97 | 3.43 |
| V6     | 96.46 | 0.28 | 0.19 | 1.25 | 2.14 | 3.58 |
| BP880  | 96.24 | 0.35 | 0.19 | 0.49 | 3.06 | 3.74 |
| BP1300 | 85.04 | 0.64 | 0.35 | 0.86 | 13.14 | 14.35 |
| BP2000 | 96.23 | 0.24 | 0.12 | 0.89 | 2.22 | 3.23 |

* Total heteroatom percentage.

### Table 2. Densities and textural parameters of carbon blacks.

| Carbon | \(S_{\text{BET}}\) (m²g⁻¹) | \(V_{\text{mi}}\) (cm³g⁻¹) | D (cm³g⁻¹) | \(V_{\text{mic}}\) (cm³g⁻¹) | \(\rho_{\text{Hg}}\) (cm³g⁻¹) | \(\rho_{\text{He}}\) (cm³g⁻¹) | \(V_{T}\) (cm³g⁻¹) | \(\rho_{\text{He}}\) (cm³g⁻¹) | \(V_{T}\) (cm³g⁻¹) |
|--------|-------------------|-----------------|------|-----------------|-----------------|-----------------|------|-----------------|------|
| SV     | 37                | 0.018           | 2.58 | 0.03            | 1.52            | 0.49            | 1.97 | 1.53            | 1.57 |
| V3     | 80                | 0.036           | 2.59 | 0.62            | 1.15            | 0.46            | 2.03 | 1.68            | 1.81 |
| V6     | 114               | 0.060           | 2.63 | 0.75            | 1.26            | 0.44            | 2.06 | 1.79            | 2.07 |
| BP880  | 224               | 0.104           | 2.58 | 0.72            | 1.07            | 0.47            | 2.05 | 1.64            | 1.89 |
| BP1300 | 511               | 0.246           | 2.58 | 0.52            | 0.74            | 0.53            | 2.16 | 1.42            | 1.51 |
| BP2000 | 1443              | 0.715           | 2.80 | 0.89            | 3.75            | 0.21            | 2.42 | 4.35            | 5.36 |

Figure 2. SEM pictures of surfaces of a BP2000 sample to show its morphology. Image (a) above at 10 μm scale and image (b) below at 20 μm.
From the data of the elemental analysis and electrical conductivity for carbon blacks (Tables 1 and 3, respectively), it can be concluded that the samples show two well-defined behaviours, the first at low pressures (25 kPa) and the second one, at higher pressures (742 kPa). At low-pressure values, there may be a competition between the aromatic structures and the porosity of the carbon material. Thus, the presence of aromatic structures, which is related to a high C/H ratio, should increase the electrical conductivity, whereas the opposite applies to the porosity. However, the increasing proximity of carbon black particles and subsequent decrease in interparticle space may explain the less important role played by the C/H ratio on the electrical conductivity of the material at high-pressure values. Finally, it should be noted that the sample BP1300 is an exception to the above behaviour, probably due to its higher content of hetero-atoms (Table 1), which may increase the electrical conductivity.

Regarding to the effects of surface chemistry on the electrical conductivity of carbon blacks, following findings were previously reported by Pantea et al. [3,4]. Electrical conductivity increased as a rule, as surface oxygen and sulphur functional groups concentration decreased. Nevertheless, several conductivities were measured in different assays with analogous concentration of those groups. In this case, conductivity raised by increasing polyaromatic character or graphitic attribute and diminishing concentration of aliphatic groups on carbon surface [3]. In view of the results obtained in this work, a total concordance with these hypotheses is observed except for the BP1300 sample. This may be due to different factors such as porosity, structure and surface groups. Thus, the BP1300 sample is the one that presents less porous development, its structure is probably formed by aromatic heterocycles containing heteroatoms of N, O and S, in greater proportion than in the rest of the samples.

3.2.2. Influence of surface area, porosity and fractal dimension

It is a fact that carbon blacks electrical conductivity is related to a number of parameters, as particle size, aggregation of particles (structure) or surface chemistry. There is increasing interest in the analysis of carbon materials electrical conductivity, as well as of several parameters, which may influence it, as it is evidenced by several researches previously reported in literature [4,5,10,50].

As it can be seen Table 2, shows two different behaviours, one for series V (SV, V3, V6) and another one for series BP (BP880, BP1300 and BP2000). Probably, these differences are due to the raw materials used, as well as to the conditions of preparation of the carbon black.

In series V, the samples V3 and V6 have similar meso-macroporous structures with low specific surface (Table 2) while that SV is fundamentally macroporous and with specific surface lower. On the other hand, the series BP presents a development fundamentally meso-macroporous with a greater contribution of microporous and specific surface that the series V (Table 2).

Other researchers [13,20,23,50,51] have previously pointed out the connection between electrical conductivity and porosity. However, conductivity depends on different parameters (porosity, surface groups, structure etc.) that contribute in different proportions. Thus, in the V series at pressures of 27 kPa, before the porous structure is destroyed, it can be seen that the porosity (V2) is very similar in all of them (1.53–1.79 cm\(^3\) g\(^{-1}\)) and is in line with very similar conductivity values (21.2–38 (Ωm\(^{-1}\))\(^{-1}\)), however in the BP series porosity (V2) varies between 1.4 - 4.35 cm\(^3\) g\(^{-1}\) and corresponds to an electrical conductivity between (7 - 34.1 (Ωm\(^{-1}\))\(^{-1}\)).

At a pressure of 742 kPa, the loss of porosity (especially of macropores, dominant pores in these carbon blacks) increases the electrical conductivity of the samples because of an increase in the contact surface of the samples.

The results of Table 2 clearly show other parameters, which may highly influence in the carbon blacks electrical conductivity. Thus, small particles of carbon black, with a higher degree of structure, or aggregation chain and lower empty space between them, will exhibit a higher electrical conductivity than carbon blacks having larger particles and higher interparticle space due to their lower aggregation. Therefore, a relationship between the aggregation degree and the electrical conductivity may be established. The degree of aggregation affects, not only the specific surface, but also to the porosity. This is due to the material internal pores and to the empty spaces caused by the contacts between particles and/or aggregated.

Table 3 includes other parameters related to the external surface of carbon blacks and/or aggregates that are in contact with the electrode. The packing density, d, for a sample of carbon black at different pressure values is associated to a lower sample volume, i.e. a loss of empty space with increasing pressure. In addition, particle size indicates the way carbon blacks are able to join in aggregates and their packaging inside the measure cylinder, whereas fractal dimension, D, is directly related to surface roughness of particles and/or aggregates. Finally, the percentage of macropores can be considered as a part of the surface of the particles or as empty space between particles and/or aggregates of carbon blacks. As can be seen from Table 3, the samples of series V show two different behaviours depending on the pressure. First, at 25 kPa of pressure, the electrical conductivity varies as follows: \(\sigma_{V3} > \sigma_{V6} > \sigma_{SV}\). By comparing samples V3 and V6, it is clear that their surface parameters (Table 3) are quite similar. This seems to indicate that the fractal dimension for sample V3 (\(D_{V3} = 2.59\), lower roughness and more points of contact between the particles) is the responsible for its higher conductivity. The samples V3 and SV exhibit similar values of D and d, while the particle size and percentage of macropores are significantly higher for SV, which may explain its lower conductivity. Conversely, at 742 kPa the electrical conductivity varied in the order: \(\sigma_{SV} > \sigma_{V3} > \sigma_{V6}\). It is possible that the packing density (d = 0.62, decrease of empty space, lower volume) and

| Carbon    | \(\sigma\) (Ωm\(^{-1}\)) | d (gcm\(^{-3}\)) | Size particle (nm) | D    | % \(V_{ma}\) | PIEC |
|-----------|----------------------|------------------|-------------------|------|--------------|------|
| SV (25 kPa) | 21.2                | 0.041            | 50                | 2.58 | 97           | 912  |
| SV (742 kPa) | 214.6             | 0.62             | -                 | -    | -            | -    |
| V3 (25 kPa) | 38                 | 0.37             | 27                | 2.59 | 63           | 315  |
| V3 (742 kPa) | 157.6             | 0.56             | -                 | -    | -            | -    |
| V6 (25 kPa) | 26.2               | 0.36             | 22                | 2.63 | 61           | 340  |
| V6 (742 kPa) | 115.4             | 0.50             | -                 | -    | -            | -    |
| BP880 (25 kPa) | 32                | 0.56             | 16                | 2.58 | 57           | 373  |
| BP880 (742 kPa) | 151.3             | 0.64             | -                 | -    | -            | -    |
| BP1300 (25 kPa) | 34.1              | 0.56             | 13                | 2.58 | 49           | 637  |
| BP1300 (742 kPa) | 251.2             | 0.69             | -                 | -    | -            | -    |
| BF2000 (25 kPa) | 7                 | 0.18             | 15                | 2.80 | 70           | 539  |
| BF2000 (742 kPa) | 44.7              | 0.24             | -                 | -    | -            | -    |
the fractal dimension ($D = 2.58$) were the responsible of the higher electrical conductivity for the sample SV ($\sigma = 214.6$ ($\Omega\cdot m)^{-1}$).

Electrical conductivity for 25 kPa was greater as follows: $\sigma_{BP1300} > \sigma_{BP880} > \sigma_{BP2000}$. The low conductivity for sample BP2000 may be related to the high value of percentage of macropores (70%) and fractal dimension ($D = 2.80$). For samples BP1300 and BP880, most of surface parameters are very similar, except for the percentage of macropores, which is lower for BP1300, and this may justify the higher conductivity measured for this carbon black. At a pressure value of 742 kPa the electrical conductivity varied in the same order observed at 25 kPa, i.e. $\sigma_{BP1300} > \sigma_{BP880} > \sigma_{BP2000}$. The high conductivity value for sample BP1300 may be related to its high packing density ($d = 0.69$ g cm$^{-3}$), which caused a greater contact between the particles and/or aggregates of carbon black.

In the isotherms obtained for the BP1300 sample subjected to 25 and 742kPa, it is observed how in the case of BP1300, an important part of its micro-meso-porous structure is destroyed, with pressure, which causes greater contact points to be obtained that favor the increased electrical conductivity. Figure 3 shows the 77K N2 adsorption isotherm for sample BP1300.

4. Conclusions

Carbonaceous materials used in this work were six carbon black materials called Sterling V, Vulcan 3, Vulcan 6, Black Pearls 880, Black Pearls 1300 and Black Pearls 2000. It can be concluded that a complete study of important parameters (chemical composition, porosity, fractal dimension, percentage of macropores, particle size and packing density) of carbon blacks to determine their relative influence on electrical conductivity has been carried out in this study.

The samples under study present aromatic structures, as a consequence of their high proportion of carbon and hydrogen in all the series.

The increase in interparticle/intraparticle porosity decreases the samples studied electrical conductivity.

Increase in conductivity with pressure may be due to a decrease in the number of holes, to an elastic or plastic deformation of the carbon beads and even to the rupture of their structure.

At low-pressure values, there may be competition between aromatic structures and porosity of the carbon material. Therefore, the presence of aromatic structures, which is related to a high C/H ratio, should increase electrical conductivity, while the opposite applies to porosity. However, the increasing proximity of black carbon particles and the consequent decrease in interparticle space may explain the less important role played by the C/H ratio in the electrical conductivity of the material at high pressures.

Figure 3. N2 adsorption isotherm at 77K, for sample BP1300.
