### 2. CARBON BLACK OVERVIEW

In order to facilitate further explanation and discussion of the obtained results, the CB model that was assumed during the fulfillment of this study will be presented. As already said, some different CB models are proposed nowadays being the common point a heterogeneous surface energy and microstructure. A small introduction about CB production and characterization techniques is presented and will be concluded by the most relevant CB properties.

## 2.1 Carbon Black Production

Carbon black is a material composed essentially of elemental carbon in the form of quasispherical particles that are fused together into aggregates. It is obtained by partial combustion or thermal decomposition of hydrocarbons. Although several kinds of CB such as channel blacks, thermal blacks, or Lampblacks can be obtained through different processes, more than the 90% of the world's annual production is achieved with the furnace black process.

In the oil furnace process, liquid fuel is injected into a flame were its partial dehydrogenation leads to CB formation. The flame itself is generally produced from natural gas. The reactor used can be divided in different units that can be described as a burner section, a furnace section, a quench section and a collection system. It has to be kept in mind that the furnace design greatly influences de type of product obtained. Fig. 2. 1 shows and scheme of a CB reactor. The hydrocarbon feedstock is injected to the flame zone after being atomized. The hydrocarbon feedstock is preferably composed of large amount of condensed aromatic compounds since the carbon/hydrogen ratio increases with the number of rings; therefore the CB yield is maximized. The oxygen content, temperature, oil rate, amount of additives, burner type and furnace geometry are carefully controlled to obtain the large number of CB grades offered by this industry. Once CB has been formed in the flame region it is passed through the furnace section at a high velocity, resulting in a residence time of the order of a millisecond. This period is crucial as it determines the physical properties of the carbon black aggregates such as specific surface area, size and surface structure which will be introduced later on in this section. Then, the reaction is shock-cooled by injecting water in the quench section reducing the temperature down to 650°C preventing also any unwanted secondary reaction.

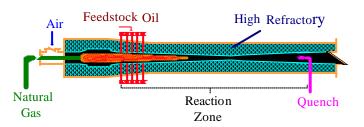
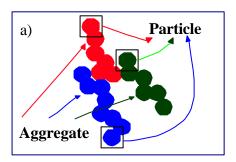


Fig. 2. 1 Scheme of the different zones of a CB reactor

# 2.2 Carbon Black Morphology

If CB is observed using Transmission Electron Microscope (TEM), it is possible to see that CB is composed of particles (ranging from 10 to 100nm) that are fused together to form aggregates. It is still unclear today, if the particles are formed first and fused later, or if the aggregate grows from an initial nucleus of similar shape. Nevertheless for furnace CB, the occurrence of single particles is practically non existent. As a result the term aggregate should be used when referring to carbon CB smallest indivisible unit and not particle, although it is widely accepted that these particles are the constituent unit of the aggregates. It was also found using different TEM projections of aggregates that they exhibit planarity, which means that their breath in a particular plane is notoriously grater than the thickness perpendicular to that plane (T. Gruber et al. 1993 and 1994a).

On the other hand, several aggregates can interact through Van der Waals forces to give place to a secondary structure known as agglomerate. Contrary to the aggregates, agglomerates are broken under mechanical stress into smaller units. Fig. 2. 2a) shows a scheme of a CB aggregate while in Fig. 2. 2b) an aggregate TEM picture can be observed.



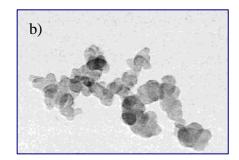


Fig. 2. 2 a) CB agglomerate scheme b) image of an agglomerate from Sid Richardson Carbon Black Co.

Since CB started to be used, many researchers have tried to characterize the material in order to understand which are the origins of CB properties.

The importance of CB characterization techniques was already stated by Medalia et al. at the beginning of 70's (A.I. Medalia et al. 1973). During this period, a significant development of new CB grades due to a headway of the furnace production method gave place to a large number of different CB grades, which clearly improved the properties of the final materials. The main problem at this point, was how to characterize properly the new CB's and find out which properties of the filler were being modified during production.

Some of the developed techniques are still used today in the industry to determine CB quality and performance such specific surface area the structure index which are here briefly described.

Specific surface area represents the area of CB per gram of material which is exposed to the surroundings and therefore is capable to interact with them. It is usually measured using adsorption isotherms. Different molecules are used to determine the specific surface area, iodine adsorption method was one of the first analysis used to specify CB specific surface. However, this method only provides an estimate of the true surface area as, b is an oxidant that may interact both chemically and physically with carbon surfaces (G. Kraus. et al.1971). The most widely accepted and commonly used measurement of surface area in research laboratories is the so-called BET method (S. Brunauer et al. 1938), based on adsorption of nitrogen at liquid temperatures (ASTM D6556-04). However, because recent studies show that nitrogen adsorption index could be affected by the energetic distribution on CB surface, it is possible to obtain similar nitrogen index for CB with different specific surface areas due to the presence of a higher number of energetic sites on one of them. This effect is clearly observed after CB graphitization as the resulting surface has diminished its number of high energetic sites (T. Gruber et al. 1994b); therefore the nitrogen index is decreased. It has to be remembered that the number of this high energetic sites would affect the CB surface activity and consequently its final performance.

The other parameter widely used to characterize CB is its structure. This parameter characterizes the empty space between randomly packed aggregates. Structure is defined by the DBP (dybutilphtalate) adsorption index (ASTM D2414-06a). This substance is gradually added to dry carbon black in an internal mixer capable of measuring the torque. An appreciable torque is not developed until the interstices between CB within an agglomerate are filled with DBP, at this moment torque rises instantaneously taking this value as the final point. Since CB networking in rubber is due to up filler-filler interactions essentially, it makes sense that the more branched the aggregates are the more difficult is to establish interactions between them and therefore the network cohesion is decreased. It should be mentioned that this test is also carried out after CB compression (CDBP) (ASTM D3493-06e1). This action induces the agglomerate breaking and it has been found that results present a higher correlation with CB properties.

However, these parameters are most times not enough to explain CB behaviour and as a consequence, other techniques have been developed during the years in order to obtain complementary information as it can be observed in Fig. 2. 3. It should not be forgotten that CB characterization involves a wide range of scales due to the presence of different order structures such as agglomerates, aggregates, particles and, as it will be presented next, structures small as 2nm that are present at the surface of CB. Therefore, it is necessary to use techniques that can cover the information located at each scale. Next the description of the most relevant CB properties found by such analytic methods are presented.

Year	Techniques	Contribution
1920	- First optical studies	
	- Transmission Electron Microscope - X-ray diffraction	- CB surface structures and geometry
1940	- BET theory	- Specific surface area studies
	- Microscope measurements on length/width ratio of CB aggregates	- Shape and structure
	- EPR techniques	- Paramagnetic Centers on CB
1960	- High resolution diffracted beam transition electron micrographs	
	<ul> <li>High resolution phase contrast electron micrographs</li> <li>High resolution Scanning Transmission Microscope</li> </ul>	- Contribution to CB models
1980	- Scanning Tunneling Microscope - Inverse Gas Chromatography - Atomic Force Microscopy	<ul><li>Surface structure elucidation</li><li>Surface activity studies</li><li>Structural studies</li></ul>
2000	<ul> <li>Neutron Scattering</li> <li>Raman Spectroscopy</li> <li>X-ray Photoelectron Spectroscopy</li> <li>Secondary Ion Mass Spectroscopy (S.I.M.S)</li> <li>Static Adsorption Isotherms</li> </ul>	<ul> <li>Porosity and bulk structure</li> <li>Carbon phases on CB (Sid Richardson model)</li> <li>Chemistry on the surface</li> <li>Chemical composition and structural deffects content</li> <li>Energy at the different phases on CB</li> </ul>

Fig. 2. 3 Evolution of the analytical techniques used for CB study

## 2.3 Carbon Black Surface Structure

At this point it is worth to look more closely to the CB surface. CB surface is composed mainly (96-99%) of carbon atoms, but what makes CB special is the structure in which this C atoms are presented.

The presence of different carbon structures on the carbon black surface was known since many years ago. Already since 1956 CB models described the presence of crystallites on the surface, which were observed by X-Ray diffraction (Franklin 1950, J.B. Donnet 1994). These first studies were also able to establish the size of the crystalline domains using the Scherrer's equation. It was found that the crystalline structure had an average width ( $L_a$ ) of 2,5nm and presented a stacking height ( $L_c$ ) which was strongly dependent to the particle size. The larger the size of the CB particle the larger the  $L_c$  value, probably due to a shorter reaction time.  $L_a$  was not found to follow any trend related to the particle size. Still today this technique is used to study the surface crystalline domains on CB. (H. Darmstadt, 2000)

Some years latter Raman Spectroscopy measurements where used to confirm the presence of different structures on CB. Using this technique, Zerda et al. where able to distinguish the two carbon structures present on CB surface. One corresponds to a structure very similar to graphite, although slightly different in the Z axis, meaning that only sp<sup>2</sup> bonds are present. The second zone, corresponds to amorphous carbon, although the exact structure of this second domain is almost impossible to describe, it thought to be composed of partially dehydrogenated polyaromatic hydrocarbons, carbon layers with numerous defects including five, six or seven member rings. Raman spectra of CB presents three peaks, two of them corresponding to the graphitic domains (1300cm<sup>-1</sup> and 1550cm<sup>-1</sup>) and the third one situated at 1500cm<sup>-1</sup> corresponds to the disordered phase. By means of deconvolution the percentage of each of these components on the carbon surface can be determined. This is an advantage as X-Ray could not determine quantitatively the percentage of the different phases. Moreover, the dimensions of the crystallites (L<sub>a</sub> and L<sub>c</sub>) can also be determined using this technique by using an empirical equation developed by Tuinstra and Koenig. This equation was obtained by means of Xray diffraction Data comparison with Raman spectra intensity (F. Tuinstra and J.L. Koenig 1970). Still today there are studies that try to proof whether this equation is valid for all crystallite ranges and carbon materials and recommendations to use XRay data to measure more precisely L<sub>a</sub> are given (A. Cuesta et al. 1998).

Other techniques such as Scanning Transmission Microscope (STM) show also the presence of different domains on CB. Based on the tunneling effect STM is able to distinguish between the presence of C with sp<sup>2</sup> or sp<sup>3</sup> hybridization. The use of this technique during the 90's by Donnet et al., who where pioneers in using this technique on CB, helped to propose their onion-like CB model composed by overlapping graphite layers

(J.B. Donnet et al. 1992). It is important to say that using this technique Göritz et al. proved that crystallite dimension  $L_{\alpha}$  decreased with decreasing particle size, contrary to the observations reported using X-Ray diffraction (Göritz et al.1999).

Another important parameter to take into account related to CB surface is its roughness, which has been related to CB interaction with polymer molecules (T.A. Virgilis et al. 1994) but also to an improvement of CB electrochemical behavior when using it as electrode in Li/SOCl<sub>2</sub> batteries (A. Le Méhauté et al. 1993). CB can be considered as a fractal object. Surface roughness has been studied by gas adsorption and also using Small Angle X-Ray Scattering SAXS. Once again the results where opposed when comparing this two different techniques. While gas adsorption shows in different studies that the fractal coefficient (parameter indicating surface roughness) was stable for all CB grades (W. Xu et al. 1996 and A. Schröder et al. 1999), SAXS experiments show an increase of surface fractal dimension with increasing surface activity (D. Göritz et al. 1999). The last author explains the difference due to a too short q-range investigated by the previous work.

At this point it is possible to have a good idea of CB surface structure. However, due to the difficulty to isolate CD aggregates to study under TEM and also due to its 2-D limitations, it was necessary to use small-angle neutron scattering (SANS) to obtain more information about the number of particles in an aggregate and its geometry. Until recently SANS techniques have played a less important role in carbon black characterization. The relevant characteristic of this technique is its capability of probing structures on length scales that are intermediate between wide angle X-ray methods and those used by most electron microscopy. Moreover due to its good penetrability this technique is very suitable for the study of bulk samples. One of the most significant studies of the microstructure and morphology of CB using SANS were performed by Hjelm et al. (R. P Hjelm, 1994). With these studies CB structure was confirmed to be formed by particles that are arranged in aggregates with an average aggregation number of 4 to 6. The main shape of the particles was represented by a prolate ellipsoid. It was also confirmed that CB presents a core-shell structure, which is formed by a shell of graphitic dens carbon and a lighter core of amorphous carbon.

Using Raman Spectroscopy results and SANS Sid Richardson Carbon Black Co. developed one of the CB model most widely accepted today (Fig. 2. 4). This model presents the aggregate as the CB aggregate composed by 4-6 primary particles whose surface is covered with graphitic (represented in black) and amorphous domains (represented in grey). It is important to say that this model was assumed to discuss the results obtained during this study.

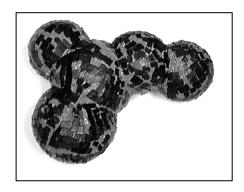
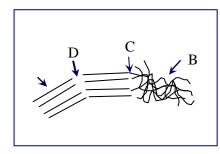


Fig. 2. 4 CB Model developed by Sid Richardson Carbon Co.

Although CB surface structure and morphology have been presented de to the relevant role on CB properties, the influence of surface energy should not be forgotten. As it will be explained next, the carbon surface structure is intimately related to its surface energy which makes it possible to have a very coherent model.

### 2.4 Carbon Black Surface Energy

In a recently developed method very precise static adsorption isotherms using ethene as adsorbate (from about 0.001 up to 1 monolayer), were used to elucidate the energetic sites and attribute them to the microstructure of the spherical primary A. Schröeder et al., 2002). Four different energetic sites where described. Graphitization, which consists in exposing CB to very high temperatures at which structural changes occur, was used in order to correlate the energetic values with the structural domains. Upon graphitization almost all CB surface structure is converted into graphitic planes while amorphous regions are vanished. The isotherms were repeated after this graphitization treatment and the energetic value for the ordered phase was easily attributed due to a steep increase in these type of sites. Graphitic regions were found to be the less energetic ones. The other three left domains correspond to amorphous carbon (with sp<sup>3</sup> hybridization) microcrystallite edges or cavities between two crystallites. Because only three different energetic sites were observed after graphitization, the absent sites were identified as the amorphous carbon. The two left sites were attributed on the basis that cavities should present higher energies as the gas molecule can interact with the surface from several directions. The different described zones and related energy can be observed in Fig. 2. 5. This energetic model clearly fits with the structure model developed by Sid Richardson Carbon Co. From lower to higher energy sites described on the filler surface are: graphitic planes, amorphous carbon, crystallite edges and cavities.



Zone	Description	Energy (kJ/mol)
A	Graphitic planes	16
В	Amorphous phase	20
C	Crystallite edges	25
D	Cavities	30

Fig. 2. 5 CB surface energy sites and their corresponding energy

The same study showed that with increasing particle size the amount of high energetic sites per gram of filler decreases dramatically showing very different surface activities to polymers. This means that the percentage of high energetic sites is not constant for the grades with different mean particle size, which leads to the conclusion that the value of specific surface area is not sufficient to describe the surface activity of the filler.

It should also be pointed out that dynamic adsorption phenomena, has also been used as basis of Inverse Gas Chromatography (IGC). Donnet et al. have demonstrated by means of finite Inverse Gas Chromatography the presence of high energetic sites on the surface of CB and how decreasing particle size promotes a higher density of these mentioned (J.B. Donnet et al. 2002). Papier et al. used the same technique to analyze the differences between graphite, CB and fullerenes, and again, high energetic zones were only found on CB surface (Papier et al. 1999). It seems then probable that these high energetic detected sites correspond to the limits between the different crystallites on the CB surface.

To conclude it can be said that CB is formed by indivisible unites called aggregates which trend to come together into agglomerates. This agglomeration tendency can be measured by means of CB structure while its interaction capacity can be measured by means of specific surface area. However, these two parameters are not enough due to the carbon structure on the surface. Crystalline regions are surrounded by amorphous domains, the proportion and size of these different structures play a very important role on the surface energy of the CB and therefore on its final behavior.

Once that the most important CB characteristics have been introduced and the CB model accepted for this wok has been presented, the several CB grades that have been used during this study are described and the reason for their selection is also discussed.

## 2.5 CB Under Study

Three different types of commercial CB were selected in order to carry out the experiments during this work. However as it is here presented some pretreatment were preformed also in some cases before plasma modification.

## 2.5.1 N-134 (Sid Richarson Carbon Co.)

This carbon black is mainly used in the tire industry as reinforcement filler mainly in truck tires due to its high abrasion resistance. It was provided by Richardson Carbon Co. The main technical data can be found at Table 2.1.

Table 2. 1 Properties of N-134

Specific Surface Area	Structure	Structure	
(BET m <sup>2</sup> /g)	(DBPA ml/100mg CB) (CDBPA ml/100mg		
137	127*	105*	

<sup>\*</sup> Sid Richardson Carbon Black Co. data.

It has to be said that specific surface area was self measured using the BET method with a Gemini V apparatus from Mcromeretics (the method is more extendedly explained in chapter 5) .On the other hand DBP and CDBP values were obtained from the mentioned sources.

On the other hand, this CB N134 was also submitted to two different pre-treatments previous to modification, these treatments are graphitization and extraction. The followed procedure to pre-treat the material and the aim of each treatment are described next.

#### 2.5.2 Extracted N-134

On one hand the surface impurities which are left on the surface of carbon black during production were extracted previously to plasma modification. The methodology used for the extraction process is based on Toluene Soxhlet extraction although more details can be found in annex 1. The objective of this pretreatment was to avoid the interaction of these impurities with the plasma and make sure that modification is happening directly on the CB surface structure.

The presence of impurities on the surface of CB is well known, already in 1968 H.B. Palmer et al. determined that most of the compounds present on the CB surface where polycycles and a minor amount of alcanes and alquenes (H.B. Palmer et al., 1968). These aromatic compounds are thought to be residues of the CB production feedstock, which as it has been previously explained is an oil with high aromaticity. More recently fullerenic structures have been detected among the extracted impurities using ToF-SIMS

experiments (Donnet et al 1999). However, the presence of these compounds on CB needs still further study.

It has been reported that after extraction carbon black presents a higher number of high energetic sites (probably crystallite edges), that were covered by the impurities molecules (M. J. Wang et al. 1991). The surface activity upon extraction has also been studied by Donnet et al. using several solvents and temperatures. Both temperature and solvent were found to be critical parameters during the extraction process. Polar organic solvents such as Toluene were found to have a higher extraction power, as it could be expected due to the aromatic nature of the CB impurities. On the other hand, high temperatures showed an increasing change in CB surface activity during a 100 hour extraction period, while at room temperature a steady state was reached already after 3 hours (A. Vidal et al. 1993). Due to the presented facts, Toluene at boiling temperature was chosen to perform the extraction of N-134.

It should be also remarked that although the presence of impurities has been studied as part of CB research, not many efforts have been done to clarify the role of the CB surface impurities in final applications such as rubber reinforcement (A. Vidal et. al 1993, J.H. Lin et al., 2002). On the other hand all the mentioned studies are mainly qualitative and very few quantitative results have been reported. In this work, the amount of extracted material was determined by weight after drying a well known volume of the extracted matter. (Further detailed information can also be found in the annex. 1)

Upon extraction of N-134 11mg of impurities per gram of CB were found. The extracted impurities were analyzed by Gas Chromatography coupled to a Mass Spectra (GC-MS) (conditions can be found at annex 2). As it was already expected, the majority of compounds were highly aromatic species. A Chromatogram showing the structures determined by GC-MS can be found in Fig. 2. 6. The most relevant compounds are pyrene, fluoroanthene, fluorene, cyclopentafenantrenone and 1,10-phenatroline,2,9-dimetyl. These compounds mentioned above except the phenantroline type were also found by J.H. Lin among others, when performing pyrolisis of several rubber CB's coupled to a GC-MS system (J.H. Lin et al., 2002).

In order to shorten the name the abbreviation N-134e will represent during this work for the extracted N-134 CB.

Table 2. 2 Properties of N-134 after extraction

Specific Surface Area	Structure (DBPA	Structure	
(BET m <sup>2</sup> /g)	ml/100mg CB)	(CDBPA ml/100mg CB)	
131	Not measured	Not measured	

As it can be observed in Table 2. 2, the specific surface area presented by N134 after extraction is slightly lower than for original N134. Although the contrary effect could be expected if more energetic sites are present on the CB surface, an explanation to this fact related to the microporosity of the impurity layer will be further developed in this work (chapter 5). Neither DBP nor CDBP were measured after this treatment, however, due to the fact that impurities only cover the structure of CB no modifications of this parameters are expected.

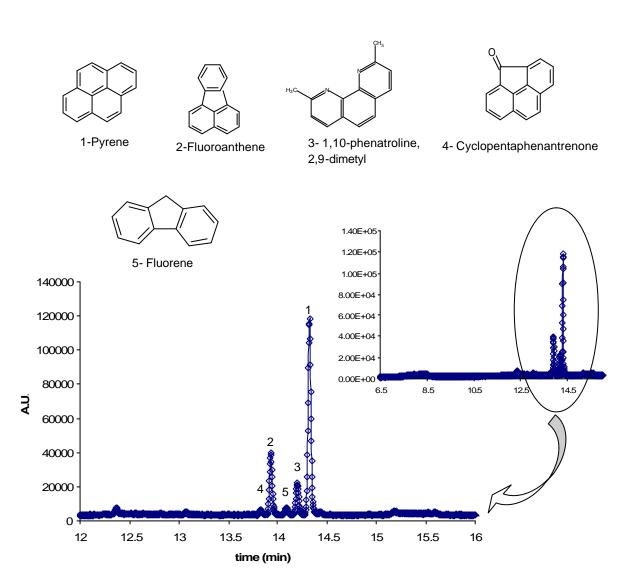


Fig. 2. 6 GC Chromatogram for the N134 extracted impurities. Identification has been done by means of Mass Spectrometry detection.

### 2.5.3 Graphitized N-134

The second pretreatment consisted in a partial graphitization of N134. When CB is submitted to high temperatures (1500-3000°C) under an inert atmosphere such as nitrogen, the CB surface structure increases its crystallinity. As a consequence the crystallites grow and the high energetic sites density decreases while the amorphous carbon disappears. This phenomena has been already studied by X-Ray diffraction and Raman Spectroscopy (T.W. Zerda 2000) showing an increase of the crystallite size (La), when the sample was allowed to cool down slowly as well as a decreasing percentage of amorphous content (T.W. Zerda, 1998). Low pressure adsorption isotherms (A. Schröeder et al. 2000) have also shown a decreasing of the area corresponding to the amorphous energy zone and a decrease in the fractal dimension showing a flattened surface. When observed by STM and WAXS not only La was also reported to increase but also Le decreased indicating growth of the crystallites in the vertical direction (G.J. Schneider et al. 2005). In accordance to this result, an increase of graphitized CB density has also been reported (W. Hess and Ch. Herd, 1993). Graphitization of Carbon black is a very useful treatment in order to better understand the influence of each carbon structure present on the surface during CB performance.

After the graphitization step CB was extracted following the same procedure as for the original N-134. In this case, the impurities found on the surface were only 10% of the original N-134 (1mg/gCB). This is an expected result as the high temperature treatment during graphitization decomposes the impurities on CB surface during the crystallite growth process. No evidence of pyrene or any other aromatic compounds were found in the GC-MS analysis of the extracted matter (Fig. 2. 7)

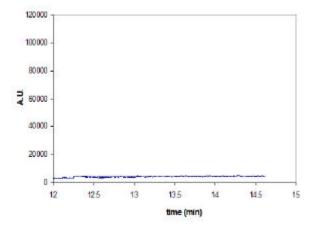


Fig. 2. 7 CG Chromatogram for N134g extracted matter (pyrene region)

As it can be observed in Table 2. 3 after the graphitization treatment, the specific surface area shows a decrease in its final value (initial value 137 m²/g). Whether it is a real specific surface area change or it is partially caused by the absence of high surface energy sites remains still unclear. Although the DBP index presents also a lower value, in this case the difference is not relevant (initial value 107 ml/100mgCB) and could lay in the error margin of the measurement. It can then be supposed that if graphitization has not changed CDBP valued it would not be changed by extraction neither as already predicted. During this work graphitized N-134 will be abbreviated as N-134g.

Table 2. 3 Properties of N-134 after graphitization

Specific Surface Area		Structure (DBPA	Structure	
	(BET m <sup>2</sup> /g)	ml/100mg CB)	(CDBPA ml/100mg CB)	
108		96 *	Not measured	

<sup>\*</sup> Measured by A. Schröder (A. Schröeder et al. 2000)

It should be mentioned that the N-134g sample used in the work of A. Schröder and the present studies is the same and therefore it is considered appropriate to use these values discussion. In the mentioned study by S. Schröder the value obtained for specific surface area of N-134g was 113m<sup>2</sup>/g which can be included in the reproducibility error margin.

The CB graphitization was carried out in order to observe whether plasma could interact with all the carbon surface structures or if the presence of amorphous carbon and high energetic crystallite edges were needed in order to modify CB.

### 2.5.4 Vulcan XC-72 (Cabot)

This CB grade provided by Cabot is mainly used to obtain high conductive rubber pieces due to its high conductivity but it is also the most used CB as support of catalysts for example in Polymeric Membrane Fuel Cell (S. Mukejee and S. Srinivasan 2003).

As it can be observed Vulcan (as will be referred from now on), has a higher surface area and also slightly higher structure than N-134 (Table 2. 4).

Table 2. 4 Properties of Vulcan XC-72

Specific Surface Area	Structure (DBPA	Structure	
(BET m <sup>2</sup> /g)	ml/100mg CB)	(CDBPA ml/100mg CB)	
220	170 <sup>1</sup> *	114 <sup>2</sup> *	

<sup>1\*</sup> Value obtained from Cabot Co. Technical Data sheet

<sup>&</sup>lt;sup>2</sup>\* Value obtained from A. Le Méhauté et al. 2003 p.25

Vulcan was also submitted to an extraction procedure, however in this case and probably due to the conditions used during production almost no impurities were found (0.3mg/g CB) (Fig. 2. 8). As it will be shown latter in this work this CB grade has a very clean surface due to the requirements of its catalytic final application.

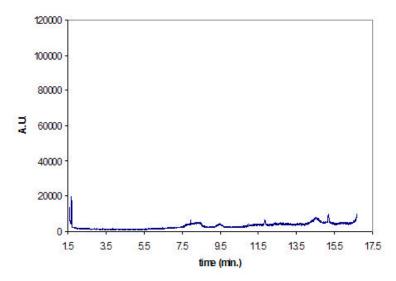


Fig. 2. 8 GC Chromatogram for Vulcan extracted impurities

## 2.5.5 XPB-171 (Degussa GmbH)

The third commercial carbon black that was used during the experiments was provided by Degussa GmbH. XPB-171 is a carbon black mainly used in inks and coatings. It is an Ultra-fine high particle size, high color furnace black. It has not only an extremely small particle size, but also a narrow particle size distribution that gives it good stability and it also makes it very suitable for use in waterborne paint systems. Technical data are presented in Table 2.5.

Table 2. 5 Properties of XPB-171

Specific Surface Area (BET m²/g)	Structure (DBPA ml/100mg CB)	Structure (CDBPA ml/100mg CB)	
656	100*	Not measured	

<sup>\*</sup> Value obtained from Degussa GmbH Technical Data Sheet

As it was the case also for Vulcan no relevant amount of surface impurities were found when the extraction was done (0.4mg/gCB), as was also bund on the technical data sheet were specifications about extractable matter with toluene after 8hr were found to be below 0,1% Fig. 2. 9.

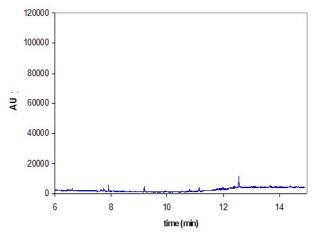


Fig. 2. 9 GC Chromatogram for XPB 171 extracted impurities

It is worth mentioning that all three CB N-134, Vulcan XC-72 and Printex where received and used in fluffy state. This means that contrary to normal CB's which are palletized, with water after production to increase their density, these CB's where not submitted to this procedure. Although fluffy CB is commercial, pelletized CB's are usually used at industrial scale due to shipping cost, safety and comfort reasons. In this case, it was thought that fluffy state was essential to be able to maximize the effect during plasma treatment.

Table 2. 6 Main characterization parameters for selected CB's

CB grade S.S.A(BET) DBPA CDBPA Extractable Ma

CB grade	S.S.A(BET)	DBPA	CDBPA	Extractable	Main impurities
	(m <sup>2</sup> /g)	(ml/100mgCB)	(ml/100mgCB)	Matter (%)	
N-134					Pyrene, fluoroanthene,
	137	127	105	1 %	fluorene,
					cyclopentafenantrenone
N-134e	131			N.D	
N-134g	108	96		< 0.1%	
Vulcan	220	170	114	0.03%	
XC-72	220	170	114	0.03 //	
XPB 171	600	100		0.04%	

To conclude it can be said that the CBs which will be modified using plasma techniques have been presented. Those CB's were selected due to the wide range of final applications (rubber reinforcement, pigments, catalysts supports) which will help to evaluate the effect of treating CB. Moreover other differences presented such as specific surface area (close related to particle size), surface structure in the case of N134g and chemical composition in terms of impurities on the CB surface (N134e) as shown in Table 2. 6, will also help to evaluate the effect of such parameters during the presented plasma treatments.

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